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Polyurethane Binder Systems for Polymer Bonded Explosives

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Defence Science and Technology Organisation**

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ABSTRACT

Polymer bonded explosives (PBXs) consist of explosive components bound together by a polymeric binder. The most common binder systems in current PBXs are polyurethane based and contain plasticisers and other chemicals that alter processability, mechanical properties and chemical stability. This report details the history of PBX binders, components of polyurethane binder systems, their properties and the procedures for obtaining the ingredients, as well as the basics of formulation, testing and quality control. Also included are details of PBX formulations on which research has been undertaken at DSTO.

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Executive Summary

Munitions with decreased sensitivity to accidental detonation (Insensitive Munitions, IM) have become a key focus in the development of explosives. The safety issues associated with the storage, handling and transportation of these weapons has led to the introduction of polymer bonded explosives (PBXs), in which the explosive components are bound together by a polymeric binder, forming a rubbery composition which is less susceptible to shock and other stimuli. The type of binder and the formulation of the PBX determine the properties of the explosive product. It is important that the system is optimised to give maximum performance, while maintaining adequate insensitiveness and hence safety.

This report is intended to be an introduction to the binder systems used in polymer bonded explosives at DSTO and a record of some of the procedures and testing involved with their formulation. It details the history of PBX binders, components of selected binder systems, their properties and the procedures for obtaining the ingredients, as well as the basics of formulation, testing and quality control. Also included are details of PBX formulations on which research has been undertaken at DSTO.

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Abbreviations

ADI	Australian Defence Industries Limited
ASM	Anti-Ship Missile
ARX	Australian Research Explosive
BHT	Butylated hydroxytoluene (2,6-di- <i>tert</i> butyl-4-methylphenol)
ButylNENA	N-Butylnitratoethylnitramine
CL-20	Hexanitrohexaazaisowurtzitane
CTPB	Carboxy-terminated polybutadiene
DHE	Dimethyl hydantoin
DMA	Dynamic mechanical analyser
DOA	Di-octyl adipate
EW	Equivalent Weight
HDI	Hexamethylene diisocyanate
HMX	Cyclotetramethylene tetranitramine, octogen
HPLC	High performance liquid chromatography
HTCE	Hydroxy-terminated caprolactone ether
HTPB	Hydroxy-terminated polybutadiene
HTPE	Hydroxy-terminated polyether
IDP	Isodecyl pelargonate
IM	Insensitive Munitions
IPDI	Isophorone diisocyanate
JPL	Jet Propulsion Laboratory, Pasadena, CA
JSOW	Joint Stand Off Weapon
MNA	N-Methyl-4-nitroaniline
NMR	Nuclear magnetic resonance
NTO	3-Nitro-1,2,4-triazol-5-one
PBAA	Polybutadiene/acrylic acid
PBAN	Polybutadiene/acrylic acid/acrylonitrile
PBX	Polymer bonded explosive
PCL	Polycaprolactone
PCP	Polycaprolactone polyol/polymer
PolyGLYN	Poly(glycidyl nitrate)
PolyNIMMO	Poly(3-nitratomethyl-3-methyloxetane)
RDX	Cyclotrimethylene trinitramine, hexogen
RS-RDX	Reduced sensitivity RDX
STS SRM	Space transportation system solid rocket motor
TPEG	Terathane [®] /polyethylene glycol
TMP	Trimethylol propane
TPB	Triphenyl Bismuth

1. Introduction

The desire for increased safety in explosives handling, storage and transportation has led to the development of Insensitive Munitions (IM). The design of these explosives and weapons decreases the likelihood of unexpected and unwanted detonation from external stimuli such as shock, weapon fragments and heat. This can be achieved by modification to the external weapons system, the explosive formulation or a combination of both. One of the more successful methods has been through the use of polymer bonded explosives (PBXs), where the explosive components are bound together by a polymeric binder, forming a rubbery composition which is less susceptible to shock and other stimuli.

Binder systems were originally developed for use with propellants and have been based on a range of polymers, including polysulfides, polystyrenes, epoxy resins and polyurethanes. The transfer of this technology to explosive applications, in the form of polymer bonded explosives, has been successful. The most common binder systems in current PBXs are polyurethane based and contain plasticisers and other chemicals that alter processability, mechanical properties and chemical stability.

This report details the history of PBX binders, components of polyurethane binder systems, their properties and the procedures for obtaining the ingredients, as well as the basics of formulation, testing and quality control. Also included are details of PBX formulations on which research has been undertaken at DSTO.

2. History of PBX Binders¹

2.1 Propellant Binders

2.1.1 Development of Binder Systems

The development of PBX binder systems was derived from solid propellant rocket technology. In 1942, a group at the Guggenheim Aeronautical Laboratory at the California Institute of Technology in Pasadena, California, developed a simple asphalt-pitch mixture - the first castable composite solid propellant. Two years later, the same group, then known as the Jet Propulsion Laboratory (JPL), trialled a binder made from a polysulfide polymer developed by a chemical company, Thiokol. This was the first liquid polymer that could be converted to a rubbery solid by a simple chemical reaction. The curing was achieved by reaction of the thiol end groups to form disulfide linkages. Many formulations were created to improve the viscosity, solids loading, ageing stability and low temperature mechanical properties of the binder. Other propellants developed during this period include compositions based on polyester, polystyrene, polyvinylchloride and epoxy resins.

¹ The history of PBX binders comes primarily from three sources [1-3].

In 1952, Thiokol, who were by then involved in the development and manufacture of solid propellant rockets, looked at liquid polybutadiene polymers for the replacement of polysulfides in an attempt to increase performance while lowering the burning temperature of the rockets. The copolymer of butadiene and acrylic acid (PBAA), which contained randomly spaced carboxylic acid groups, was found to react with an epoxide resin to produce a cured binder. This provided increased specific impulse (a measure of propellant burn rate efficiency) and improved mechanical properties, with the exception of poor tear strength. This was rectified by the addition of acrylonitrile to give a polymer consisting of polybutadiene, acrylic acid and acrylonitrile (PBAN). This polymer soon became extensively used in propellant formulations such as TP-H-1011, used in STS SRMs (space transportation system solid rocket motors), with total production of PBAN exceeding that of all other solid propellant binder compositions for several years after its initial inception.

In the late 1950s, Thiokol developed a polymerisation technique that resulted in the carboxyl groups being situated at the end of the butadiene chains, forming carboxyl-terminated polybutadiene (CTPB). This polymer was cured with an imine/epoxide combination and formed propellants with improved mechanical properties without affecting the specific impulse, density and solids loading. CTPB formulations were used in propellants from the early 1960s. In 1966, CTPB-based propellant TP-H-3062 was used in the Surveyor retro motor for the first soft moon landing.

2.1.2 Polyurethane Binder Systems

During the early 1950s, production of polyurethane binder systems commenced and they were found to give a reproducible, clean cure. Polyethers were formed from high molecular weight glycols, with hydroxyl groups at both ends, which were then cured with diisocyanates. The main problems such as low temperature crystallisation, moisture sensitivity and non-ideal ageing properties were improved by the addition of chemicals, e.g. plasticisers, bonding agents and antioxidants. Even with these improvements, the carboxylated polybutadiene/epoxide formulations still remained more popular. In the 1960s, hydroxy-terminated polybutadiene (HTPB) was developed and the first test in rocket motors in 1972 showed advantages over CTPB, including higher strain capacity at low temperature and better ageing properties. It has since become the most widely-used polymer in polyurethane propellant binders, with excellent mechanical and increased IM properties.

2.2 Explosives Binder Systems

Research on composite propellants binders was also applied to explosive formulations. The first PBX was developed in Los Alamos in 1947 and utilised a polystyrene binder. It also contained a plasticiser to improve the mechanical properties. Since then there have been a range of binder systems developed based on fluoroelastomers, polyvinylchloride and CTPB, among others. The polymers most widely used in current PBX formulation are polyurethanes.

3. Polyurethanes

Polyurethanes are organic polymers with carbamate (urethane) linkages. They are used commercially in a wide range of foams, rubbers and plastics of varying densities and hardness for products such as varnish, glue, insulation, packaging and automobile parts, including tyres.

Polyurethanes are formed from the reaction of di- or multi-functional isocyanates with polymeric diols, often referred to as prepolymers (Figure 1). Two difunctional components form linear polyurethanes which become entangled, but are not chemically bonded to each other, and so the product has relatively low mechanical strength. If improved mechanical properties are desired, chemical cross-linking between the polyurethane polymers is required. This can be achieved by selecting a multifunctional alcohol or isocyanate or, alternatively, by adding other chemically reactive ingredients.

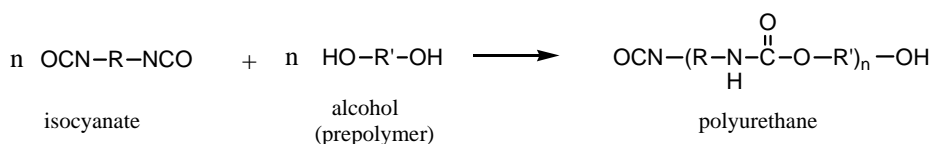


Figure 1. Formation of polyurethanes

Isocyanates also react with water or amines to form ureas (Figure 2).

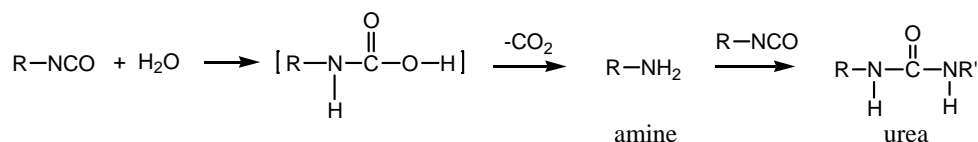


Figure 2. Reaction of an isocyanate with water

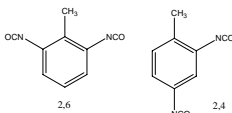
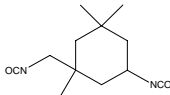
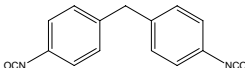
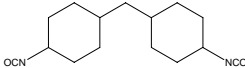
The curing of polyurethanes occurs as the urethane bonds form and the time required for the reaction to be completed can range from minutes to days depending on the components and the curing temperature. One group of polyurethanes containing blocked polyisocyanates needs to be activated by heat to initiate curing. Other one-component systems are cured with atmospheric moisture.

The rate of curing is linked to the pot life, which is the time during which the polyurethane can be manipulated before cross-linking leads to increased viscosity and curing. The desired pot life is dependant upon the use to which the polyurethane is put.

There are several aliphatic and aromatic diisocyanates, as well as many alcohols containing various functional groups, that can be used in the formation of polyurethanes. Each system provides different properties such as varying curing time, hardness, UV stability, weatherability, gloss properties and chemical resistance. Bayer has produced a document on the chemistry of polyurethanes that is a useful reference [4]. Some of the more common, commercially-available diisocyanates are listed in Table 1.

Isocyanates are toxic and should be handled with care, particularly monoisocyanates, which have low boiling points and are easily inhaled. Monoisocyanates are present as impurities in low concentration in most diisocyanates.

Table 1. Common diisocyanates

Isocyanate	Structure	B.p. (°C) /pressure (torr)	Major producer
Toluene diisocyanate (TDI)		253/760	Bayer
Hexamethylene diisocyanate (HDI)	$\text{OCN}(\text{CH}_2)_6\text{NCO}$	130/13	BASF, Bayer, Olin
Isophorone diisocyanate (IPDI)		153/10	BASF, Bayer, Huls, Olin
Diphenylmethane-4,4'-diisocyanate (MDI)		196/5	Bayer
Bis(4-isocyanatocyclohexyl)methane (hydrogenated MDI, HMDI)		179/0.9	Bayer

4. PBX Formulations

4.1 PBX Binders

4.1.1 Polyurethane Component

The most widely-used binder systems in the propellant and explosive industries are polyurethane binders based on the hydroxy-terminated polybutadiene prepolymer (HTPB, Figure 3a). These formulations have outstanding mechanical properties, hydrolytic stability, ageing stability, and desirable viscosity and solids loading. HTPB systems are also the most common binder systems utilised in DSTO PBX research. HTPB is formed from free radical polymerisation of 1,3-butadiene, which leads to some branching and formation of a polymer with a hydroxyl functionality of approximately 2.2-2.4. It can therefore be used with a range of di- or multi-functional isocyanates, but is

often combined with isophorone diisocyanate (IPDI), using dioctyl adipate (DOA) as a plasticiser.

The HTPB polymer that is commonly used in PBX formulations has three forms, all having a molecular weight of approximately 2800. R-45M is a high-quality military grade polymer which is made by a batch process. This level of quality is not required for general PBX formulation. R-45HT, a commercial grade made in a continuous process, is used in most systems and is within the HTPB Type II limits that are specified for formulations such as PBXN-109 [5]. Another difference between the two is that R-45HT has a higher viscosity and hydroxyl functionality than R-45M. Recently, R-45HT has been replaced by R-45HTLO, a low-odour version that is essentially the same polymer mix, with a slightly lower hydroxyl value. Compared to R-45HT, R-45HTLO has been found to increase the curing rate of formulations, leading to a decrease in the required catalyst levels.² An increase in hardness has also been observed, possibly due to a higher level of cross-linking. Due to restrictions in the US, obtaining HTPB can be time-consuming. Detailed in Appendix A is the most efficient procedure for ordering HTPB.

Hydroxy-terminated polyethers (HTPE, Figure 3b) are another common group of prepolymers. The HTPE used in many PBX formulations is a copolymer of poly-1,4-butanediol (poly-THF or Terathane®) and polyethylene glycol (PEG), also referred to as TPEG. TPEG is difunctional and reaction with a difunctional isocyanate does not lead to cross-linking. For this reason, it is often used with Desmodur N-100,³ an isocyanate mix containing the multifunctional biuret of hexamethylene diisocyanate (HDI, Table 1) (Figure 3c). HTPE can be used in formulations containing energetic plasticisers, whereas HTPB is immiscible with such plasticisers. Combined with the higher density of HTPE, this allows higher energy formulations to be created. HTPE has also been reported to increase IM properties in propellants by reducing response to cook-off and impact stimuli in comparison to a HTPB formulation [6].

Hydroxy-terminated caprolactone ethers (HTCE, Figure 3d), also known as polycaprolactones (PCL) or polycaprolactone polyols (PCP), also have potential in polyurethane systems and have previously been evaluated in some propellant and explosives systems [7-9]. The advantages of using HTCE are its low cost and commercial availability and that it can be used in formulations containing energetic plasticisers. Dow has a wide range of polycaprolactones, to suit many applications, marketed as TONE™ polyols, while Solvay has an extensive selection under the CAPA® trademark. Research using CAPA 7201A, a low melting diol formed from 2-oxepanone and poly(1,4-butyleneglycol), is planned at DSTO.

Energetic binder systems containing nitrated prepolymers, such as polyGLYN (poly(glycidyl nitrate)) or polyNIMMO (poly(3-nitratomethyl-3-methyloxetane)), can be used to enhance performance over formulations containing inert polymers, but will not be discussed here. For further information refer to the review and study by Provatas [10, 11].

² Preliminary observations from DSTO laboratories.

³ N-100 can be difficult to obtain, and this process is outlined in appendix A.

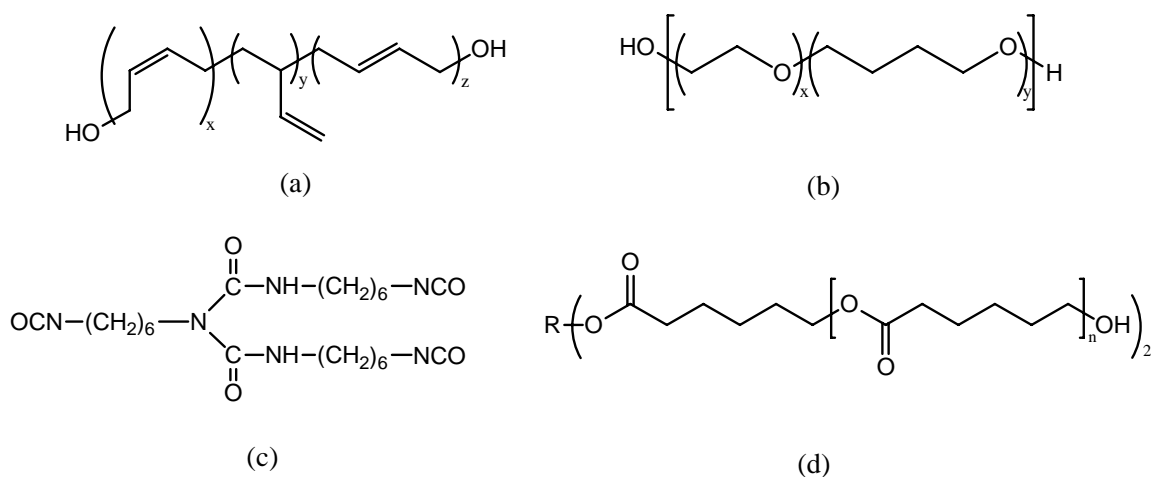


Figure 3. Common polyurethane components: a) hydroxy-terminated polybutadiene (HTPB), b) hydroxy-terminated polyether (HTPE), c) Desmodur N-100 and d) hydroxy-terminated caprolactone ether (HTCE).

4.1.2 Additional Binder Ingredients

Also included in the binder systems are components added to improve mechanical properties, assist in curing and increase the stability of other components and/or the product. These include bonding agents, wetting agents, cross-linkers, plasticisers, antioxidants, stabilisers and catalysts.

The mechanical properties of the binder are altered by the addition of a plasticiser, which imparts the rubbery characteristic that is required for IM, reduces the viscosity for ease of casting and enables higher solids loading. Plasticisers are also used to alter the glass transition temperature, the temperature at which the binder changes from rubbery to brittle. The glass transition occurs when movement of molecules in the system is restricted due to low temperature and the resulting brittleness may have serious implications for the IM properties of an explosive. All of these properties can be varied with plasticiser selection. Dioctyl adipate (DOA) is a commonly used plasticiser, providing a good balance of desired properties. Other plasticisers include isodecyl pelargonate (IDP), dioctyl sebacate and a range of phthalates. Energetic plasticisers such as N-butylnitrateethyl nitramine (butylNENA,⁴ Figure 4a) can be added to improve performance over conventional plasticisers.

Mechanical properties can also be optimised by altering the physical or chemical interactions between the components in a formulation. Bonding agents, such as Dantocol DHE, are used to enhance interface strength between the binder and solids by adsorbing onto the filler and forming chemical bonds with the binder. The major component of DHE is N,N-di(2-hydroxyethyl) dimethyl hydantoin (Figure 4b), which forms chemical bonds with the isocyanate through its hydroxyl groups and interacts with nitramines such as RDX and HMX via the amide groups. Wetting agents, such as Lecithin, also increase the

⁴ ButylNENA can be difficult to obtain, and this process is outlined in appendix A.

interaction between binder and filler - by reducing the surface tension of the liquid component, which allows the liquid to spread over the surface of the solid and wet it. Cross-linkers, e.g. trimethylolpropane, a trifunctional alcohol, form additional chemical bonds within the polyurethane system and improve mechanical properties.

The curing rate of polyurethanes is largely dependant upon the isocyanate used and is often too slow for explosive applications. Formulations that include isocyanates that cure relatively slowly, e.g. IPDI, incorporate catalysts to increase the rate of curing. Triphenylbismuth (TPB) and dibutyltin dilaurate (DBTDL) are two catalysts that are commonly used. It has been noted in our laboratories that when the catalyst is added to the prepolymer and the mixture is left for more than a few hours, the curing time, after addition of the isocyanate, decreases. This is likely due to the activation of the hydroxyl groups, with the effect increasing over time.

The quality of the ingredients and the stability of the final product in regards to safety are very important. Antioxidants are added to PBX formulations to inhibit oxidation of the binder, which causes extra cross-linking and hardening and may form a brittle product with possibly lower IM properties. Some of the components of PBX formulations, particularly nitrate esters, contain stabilisers, e.g. ethyl centralite, to increase shelf life. ButylNENA contains 0-1% N-methyl-4-nitroaniline (MNA) to scavenge free radicals that may catalyse a reaction or decomposition. HTPE also contains a stabiliser, 2,6-di-*tert*butyl-4-methylphenol (butylated hydroxytoluene, BHT), in small amounts (0.05-0.2%).

All of the binder ingredients are mixed to give a product with the desired stability and mechanicals properties, both for casting and in the cured product. Some useful properties and safety data of the most commonly used compounds are included in Table 2.

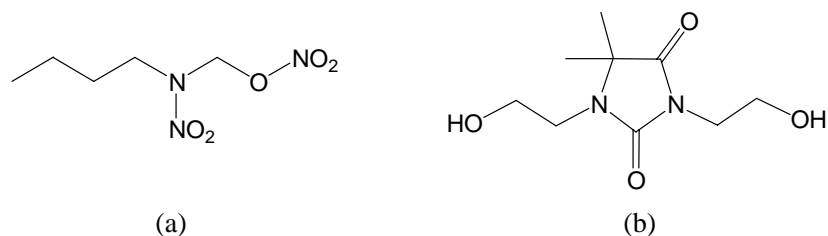


Figure 4. Polyurethane binder ingredients: a) butylNENA and b) DHE

4.2 Other PBX Ingredients

As well as the binder and its components, PBX formulations also include the explosive itself, e.g. RDX, HMX, CL-20, NTO, and often other ingredients such as a metal or oxidiser. Aluminium is used as a fuel to increase blast effects. This is achieved by causing additional, higher-temperature burning after the initial detonation, once the aluminium becomes exposed to the oxygen in the air. Formulations that contain aluminium in high proportions, used specifically to increase the duration of the blast, are referred to as enhanced blast or thermobaric explosives. An oxidiser, such as ammonium perchlorate, can be used to increase the oxygen content and rate of burning. PBXs formulated for

Table 2. Common binder components and their properties

Component and CAS No.	Type	Equivalent weight (g/eq.) Av.	Functionality	Density (g/ml) at °C	Viscosity at °C	Melting Pt. (°C)	Safety notes	Source and cost (as of 2006)
Isophorone diisocyanate (IPDI) 4098-71-9	Diisocyanate	111	2 NCO 37.5% NCO	1.06/20	10mPa.s /25	-60	Toxic. Moisture sensitive. Skin & eye irritant	Aldrich \$286/L 98%
N-100 (HDI biuret)	Multifunctional isocyanate	191	22% NCO	1.14/25	7500mPa.s/25	<-5	Toxic. Moisture sensitive	Bayer - free sample, shipping approx. \$240
HTPB (R-45HTLO)	Multifunctional diol	1101	2.4-2.6 OH	0.90/23	8000mPa.s/23	-75 (glass transition)		Sartomer (Atochem) \$55/kg
HTPE	Diol	1501	2 OH	~1.0/25	1100mPa.s/50	-4→13		Alliant (ATK)
HTCE (CAPA 7201A)	Diol	1008	2 OH	1.03/35	300mPa.s /50	30-35		Solvay \$11/kg
Diocetyl adipate (DOA) 103-23-1	Plasticiser	n/a	n/a	0.920/25	13.7mPa.s /20	-67		Aldrich \$112/L 99% Fluka \$40/L >97%
Isodecyl pelargonate (IDP) 109-32-0	Plasticiser	n/a	n/a	0.864/25	4.15mPa.s /40	-73		Fisher
Butyl NENA 82486-82-6	Energetic plasticiser	n/a	n/a	1.121/25	<20mPa.s /20	-9→27	Explosives Class 1.3	DYNO-Nobel \$130/kg NSWC-IH \$122/kg
Triphenylbismuth (TPB) 603-33-8	Cure catalyst	n/a	n/a	1.59/20	White powder	75-79	Moisture sensitive	Aldrich
Dibutyltin dilaurate (DBTDL) 77-58-7	Cure catalyst	n/a	n/a	1.07/25	Data not available	22-24	Respiratory/eye irritant. Harmful	Aldrich \$56/100g Fluka \$190/500mL
AO 2246* 119-47-1	Anti-oxidant	n/a	n/a	1.08/20	Yellow powder	125-128		Aldrich \$120/500g
Dantocol DHE 26850-24-8**	Bonding agent	112	2 OH	1.22/25	11650mPa.s /25	17.5		Lonza - through Interchem, Melb.
Trimethylolpropane (TMP) 77-99-6	Cross-linking agent	45	3 OH	1.09/25	White waxy solid	59	Flammable, absorbs moisture	Aldrich \$33/500g 97% Fluka \$48/kg >98%
Lecithin	Wetting agent	n/a	n/a	1.03/25	Solid	236		Fisher
N-methyl-4-nitroaniline (MNA) 100-15-2	Stabiliser	n/a	n/a	1.20/25	Gold crystalline powder	149-151	Toxic, irritant	Aldrich \$78/25g
Ethyl centralite 85-98-3	Stabiliser	n/a	n/a	1.12/25	Powder	79		

n/a not applicable

*2,2'-methylene-bis(6-tert-butyl-4-methyl phenol)

** CAS No. of major component

underwater explosives utilise both aluminium and an oxidiser – the aluminium releases extra energy, while the oxidiser provides a ready supply of oxygen to the aluminium that it needs in order to burn efficiently.

4.3 Effect of Ingredients

All of the different ingredients in the formulation have an effect on both the binder system and the properties of the final explosive and must be taken into account. Before any material not previously used in a formulation is added, tests must be carried out to determine the compatibility of the new ingredient with other components of the mix. Vacuum stability tests (see section 6.1.2) are used to determine if a reaction is occurring by measuring the amount of gas released over a period of time. Once the stability is confirmed, studies must be carried out to determine the effect of the new ingredient on the properties of the formulation, e.g. viscosity, density, decomposition temperature, glass transition temperature.

The mechanical properties of an explosive formulation are easily altered by varying the proportion of plasticiser, binder and solids. A good formulation should give a viscous mix which is castable and cures to a rubbery composite without the settling of solids and without migration of the plasticiser. The particle size of solids also affects the viscosity of the PBX. The amount of solid that can be added to the mix while maintaining the desired viscosity is dependant upon the density, shape and size of the ingredients, although the viscosity of the formulation can then be optimised by altering the binder content.

To obtain an explosive formulation with the desired properties, the ratio of ingredients must be optimised, although this often means sacrificing properties in one area to increase those in another. There must be a compromise between processability, pot life, castability, mechanical properties and the desired explosive performance properties in order to arrive at a formulation that is acceptable for the intended use of the explosive.

4.4 DSTO Research

Some of the PBX formulations on which research has been undertaken at DSTO include:

- PBXN-109 for Penguin ASM [12-14]. This explosive contains 16% HTPB/IPDI-based binder, 64% RDX (explosive) and 20% aluminium and is a well-characterised in-service PBX. The binder also contains DHE, DOA, AO 2246 and TPB. The formulation (Table 3) was developed in the US (MIL-E-82886(OS)[5]) and has been evaluated at DSTO, including formulations using CMX-7 (plasticiser desensitised RDX) and ADI RS-RDX (reduced sensitivity RDX).
- PBXW-115 (Aust) for underwater use [15, 16]. This formulation contains 20% RDX, 25% aluminium, 43% ammonium perchlorate and 12% binder, consisting of 5.7% HTPB, 0.54% IPDI, 5.7% isodecyl pelargonate, 0.05% antioxidant and 0.004% dibutyltin dilaurate. The formulation is nominally the same as the US PBXN-111, but uses RDX produced in Australia by ADI.

- Energetic binder systems [10, 11]. These serve to increase the effectiveness of the explosive by replacing inert binder materials with energetic materials such as energetic plasticisers (butylNENA) or prepolymers (polyGLYN, polyNIMMO). The isocyanates in these systems are IPDI and/or N-100. ARX-3010 is an enhanced blast explosive developed at DSTO containing butylNENA with a HTPE/IPDI/N-100 polyurethane.
- Evaluation of reduced sensitivity RDX in PBXW-115(Aust) [17], ARX-2014 and ARX-2020. ARX-2014 has the same formulation as PBXN-109, but uses RS-RDX, while ARX-2020 uses the same binder ingredients, but is a non-aluminised formulation.

US formulations have exact specifications that each of the ingredients must comply with. These can be found in the appropriate military specifications which are contained in the US Military Standards Fulltext database[18] available through the DSTO library.

Table 3. Formulation of PBXN-109

Ingredients	Nominal weight %
RDX	64.00
Aluminium	20.00
Hydroxy-terminated polybutadiene (HTPB)	7.346
Diocetyl adipate (DOA)	7.346
Antioxidant 2246 (AO)	0.10
N,N 2-Hydroxyethyl dimethyl-hydantoin (DHE)	0.26
Triphenyl bismuth (TBP)	0.02
Isophorone diisocyanate (IPDI)	0.9465

5. Binder Curing

5.1 Curing Times

In explosive and propellant formulations, the isocyanate component is generally added last to ensure adequate mixing time before curing begins and also to avoid premature curing from exposure to moisture. The pot life of experimental formulations only needs to be 1-2 hours to allow for mixing and casting of the explosives - it is the mechanical and explosive properties that need to be optimised at this time. In industry, this time has to be extended to 3-4 hours to allow for the filling of multiple large items. The curing cannot be delayed for too long because settling of solids may occur. The curing process generally takes place at elevated temperature (60°C) over seven days.

5.2 Mix Quantities

The reactive curing components of the formulation are usually mixed in an isocyanate to alcohol proportion of 1:1 to ensure full curing. Sometimes this ratio is increased, up to 1.2:1, to alter the mechanical properties of the product. Other ingredients such as bonding agents also need to be included in this calculation as they contribute to the hydroxyl

equivalent of the reaction. The calculation of these quantities is based on the equivalent weight (EW) of each component.

The equivalent weight of a compound is the molecular mass divided by its functionality, i.e. the number of isocyanate groups in IPDI or the number of hydroxyl groups per HTPB polymer. Usually, the exact mass of a polymer is unknown and the equivalent weight has to be determined by titration or NMR methods. Procedures for determination are contained in appendix B.

Other commonly used terms are the hydroxyl number or hydroxyl value, which are also terms to describe the functionality of a compound. OH number is in mg KOH/g, is determined by titration and is related to equivalent weight by the equation:

$$\text{EW (g/eq)} = \frac{56.1 \text{ mg KOH/eq} \times 1000 \text{ mg/g}}{\text{OH number (mg KOH/g)}}$$

OH value is in meq/g, and is related to equivalent weight by:

$$\text{EW (g/eq)} = \frac{1000 \text{ meq/eq}}{\text{OH value (meq/g)}}$$

5.3 Calculations

When determining the correct amount of each binder ingredient, it is the reactive polyurethane components, known as curatives, that need to be calculated accurately to ensure a successful cure. Other binder components such as plasticisers and antioxidants do not react significantly and so are subtracted from the total binder amount to give the percentage of curatives (%C) in the total formulation, i.e. isocyanate + alcohol + bonding agent/cross-linking agent.

Given the equivalent weights (EW) of the polyurethane components and the percentage of binder in the formulation, it is possible to calculate the amount of each curing agent needed for a successful cure. In a simple two-component mix containing only an isocyanate and a hydroxyl polymer, the equation below is adequate:

$$\% \text{ of component in formulation} = \frac{\text{EW of component}}{\text{Sum of EW's}} \times \% \text{ curatives in formulation}$$

where the percentages are by weight.

When other ingredients that will react with either the hydroxyl groups or isocyanates that are present are involved, e.g. DHE, TMP or N-100, the calculations becomes more complicated. Generally, the amount of this ingredient in the total binder is a nominated amount or ratio and, with this known quantity, the isocyanate and alcohol quantities can be calculated to make a formulation with a set binder amount.

The amount of each component in the curing system is calculated as above, except that the ratio of components is no longer 1:1 and must be taken into account using simple algebra.

For example, a curing system containing IPDI (NCO part), DHE (OH part) and HTPB (OH part) needs to be mixed at a NCO:OH ratio of 1:1. Let IPDI = 1 equivalent, then DHE + HTPB = 1 as the ratio to NCO:OH must be 1:1. The % DHE is known (given), as can be denoted as χ equivalents, then % HTPB = $1-\chi$ equivalent. These equivalents can then be applied to the general equation above and the % DHE can be used to find χ , which can then be substituted back into the equations to find the amounts of IPDI and HTPB. Some example calculations can be found in appendix C.

6. Binder Testing

6.1 Testing of Binder Systems

6.1.1 Mechanical Testing

The mechanical properties of a binder system are used to compare formulations and determine their suitability for an application. PBX binders need to be relatively hard, rubbery and have a low glass transition temperature (generally $<-50^{\circ}\text{C}$).

Hardness – PBXs are measured using ASTM-D2240 method for Shore “A” hardness using a Shore A-2 durometer and generally require a hardness measurement above 40. The binder alone is tested using a Shore O durometer, which is designed for softer materials.

Tensile strength, shear testing, elongation at break – these properties are measured using a materials testing machine (Instron) or dynamic mechanical analyser (DMA), which give stress and strain readings. If these measurements are taken over a range of temperatures (-120°C to 100°C), they can be used to determine the glass transition temperature. The glass transition temperature is not a well-defined temperature like a melting point and varies with heating or cooling rate.

Density – generally measured using a helium pycnometer. Another technique used to measure the density is the Archimedes principle, where the weight of the object is measured in air and then again in water and the density calculated from the difference. Density can be used to determine if settling of solids is occurring in a formulation.

6.1.2 Thermal Analysis

If a component or mixture of components is unstable due to heat or if ingredients are incompatible due to undesirable reactions that occur between them at elevated temperatures, decomposition often leads to the formation of gases, usually CO_2 . Measurement of the amount of gas evolved, changes in state and loss of mass give an indication of the rate of reaction.

Vacuum stability – duplicate samples are placed in glass test tubes, evacuated and heated. After one hour at 100°C (to reach equilibrium) the volume of gas evolved is monitored over 40 hours at 100°C. If the total amount of gas evolved is greater than 2 mL/g more than that given off by the individual components, the ingredients are deemed incompatible and should not be used together in a formulation.

Thermal stability – assessed using differential scanning calorimetry (DSC) to give decomposition temperature and phase/glass transition temperature, and thermal gravimetric analysis (TGA) to measure mass loss at elevated temperatures.

6.2 Quality Control

The equivalent weight of a polymer varies with each batch and so all new prepolymer arrivals are tested for hydroxyl content to determine the equivalent weight for that batch. This can be done by titration or NMR methods, but it should be noted that if the results from the two methods differ, the titration results are taken, as they are generally more reliable and reproducible. An accurate equivalent weight ensures that the quantities of the binder components added to subsequent mixes are calculated correctly to give a fully-cured product. In addition, the equivalent weight determines if a polymer is suitable for use in a formulation with particular ingredient specifications. The quality of prepolymers can also be examined by measuring dynamic viscosity.

The equivalent weight of new batches of isocyanate and other components that participate in the urethane bonding should also be determined where appropriate (see Appendix B for method). Compounds that are pure, such as IPDI, which is >99% pure monomeric diisocyanate, will have a low-variable EW, while components, such as N-100 and DHE, contain mono- and di-functional compounds other than the major ingredient and will have a more variable EW. The isocyanate content as a percentage can also be measured to ensure that it complies with specifications.

Other tests that can be used to determine the quality of components include refractive index (DHE), melting point (TPB), density, viscosity, acidity, moisture content and appearance.

Most of the components of PBX formulations are quite stable with the exception of the isocyanates. They react readily with moisture to form a hard, cured solid and should be stored under nitrogen. N-100 is particularly sensitive and, according to the manufacturer, has a shelf life of approximately six months from date of manufacture. The cure catalysts may also absorb moisture and should be stored appropriately.

The stabiliser contained in some components is consumed and the concentration will decrease over time. In these cases, the amount of stabiliser is monitored by HPLC or NMR to determine when the binder or other component is no longer reliable to use. For some ingredients additional stabiliser can be added to maintain a suitable level. Once the binder has been cured this is no longer possible.

7. Conclusion

This report has given an overview on the use of polyurethane binder systems in explosive formulations with a focus on the systems at DSTO. The information presented is intended to act as a base for those who are involved in cast-cured PBX formulation to build upon. This introduction to binder ingredients, formulation, calculations and analysis should provide a basic understanding and contains useful references and data not otherwise readily available.

8. Acknowledgements

The majority of unreferenced information in this report comes from the knowledge and experience of Mr Brian Hamshere (who recently retired), with input from Dr Ian Lochert.

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Appendix A: Ordering Information

HTPB

R-45HTLO is the HTPB polymer currently available through Sartomer in the US.

The Australian contact is John Mccarry, John@TRChemicals.com.au
TR Chemicals
195 Briens Road
Northmead, NSW 2152, Australia
(02) 9630 7655

Export of this product is regulated by the United States Department of Commerce and a licence must be obtained. The export licence should be obtainable by the supplier, but it may be useful to contact the Australian Embassy to speed this up. Import into Australia has no such restrictions.

N-100

Bayer N-100 samples can be obtained, generally free of charge, but covering the cost of shipping, by contacting:

Anthony Noonan
Product Manager
Bayer Hodgsons
Homebush Bay NSW
(02) 8748 3930

Shipping cost for 1 kg is approximately \$240

ButylNENA

Norway - DYN0-Nobel

Classed as 1.3C and must be shipped in an explosives shipment (\$10,000-\$15,000 for transport).

Contact: Erland Skjold, erland.skjold@eu.dynonobel.com, or
Harald Bergsvaag, harald.bergsvaag@eu.dynonobel.com

US - Indian Head

Class 9 dangerous goods, can be shipped through a freight company that handles dangerous goods.

Contact: Charles Painter (Chuck) charles.r.painter@navy.mil

Cost for 20 kg (45 pounds) = \$54/pound x 1.105 govt. surcharge = \$2,685 + \$500 shipping to DSTO Edinburgh.

Documentation needed:

- End users statement from DSTO
- Foreign Military Sales (FMS) document - needed when the goods are moving from US Govt. to Australian Govt. If it's an FMS, there is no need for an export licence.

Contact: The Australian Embassy in Washington. Currently this is Ian Donald (FMS Ops Manager), ian.donald@defence.gov.au

Appendix B: Determination of Equivalent Weight

B.1. Titrametric Method for the Determination of Hydroxyl Equivalent Weight

The procedure involves the base-catalysed acetylation of polymers containing terminated hydroxyl groups, using acetic anhydride. The excess acetic anhydride is hydrolysed with water and the liberated acetic acid is titrated against 0.5 N alcoholic potassium hydroxide solution.

The following solutions are required:

1. Acetic anhydride (prepare daily): Mix 12 mL acetic anhydride with 72 mL pyridine.
2. Ethanolic (or methanolic) 0.5 N potassium hydroxide: A standardised 'VOLUCON' potassium hydroxide (N/10) is poured into a 200 mL volumetric flask and topped up with methanol. Shake and leave to stand.
3. Phenolphthalein (1%): Dissolve 1.0 g phenolphthalein into 100 mL 1:1 aqueous pyridine.

Procedure:

Polymer analysis is to be carried out in triplicate (with 3 blanks).

1. Accurately weigh out 2 grams a sample into a wide-neck 250 mL glass stoppered flask.
2. Add 5 mL of the acetic anhydride solution to each sample, using a volumetric pipette. A uniform drainage time must be employed.
3. Moisten glass stopper with pyridine, place loosely in the flask and set on steam bath for 2 minutes, loosening stopper 2-3 times.
4. Tighten stoppers and heat on water bath for 2 hours.
5. Remove flasks from bath, cool for 3 minutes (loosen stoppers) and add 5 mL distilled water to each flask, washing down stopper and walls of flask.
6. Place flasks back onto steam bath for an additional 2 mins.
7. Remove flasks and allow to cool at room temperature for 15 minutes.
8. Add 25 mL of isobutyl alcohol, washing down stopper and flask walls, and 15 mL of toluene to each flask and mix well.
9. Add 0.5 mL of phenolphthalein solution.
10. Titrate solutions with 0.5 N methanolic potassium hydroxide solution until the first faint pink end point permanent for 15 seconds and record titre values at the end point.
11. Run a blank determination in the same manner, omitting the sample. If the titration of the sample is less than 65% of the blank, repeat using a smaller sample.

Equivalent weight numbers and functionality are determined from the following:

$$\text{OH Eq. Wt.} = \frac{(\text{wt. of polymer}) * 1000}{(V_{\text{blank}} - V_{\text{sample}}) * N}$$

Where N = the normality of the potassium hydroxide solution.

$$\text{Functionality} = \frac{56100}{\text{OH Eq. Wt.}}$$

B.2. NMR Spectroscopic Method for the Determination of Hydroxyl Equivalent Weight

The procedure described here involves the use of carbon-13 NMR spectroscopy, with a suitable relaxation agent (chromium acetylacetonate), to accurately measure equivalent weight numbers for hydroxy-terminated polymers.

Procedure:

1. Preheat polymer to 60°C.
2. Weigh 2.0 g into a 5 mm NMR sample tube
3. Add 0.075g polyethylene glycol 4000, 0.070 g chromium acetylacetonate and 3.8g CDCl₃.
4. Shake tube well, sample is now ready for NMR analysis.
5. Run ¹³C NMR spectral analysis under following conditions: (guide only)
O1=14900, O2= 4650, SW = 15151.515, NS=18000, D0=2.46S, D1=9.0uS D3=16uS
LB=2.0.
6. Collect scans and process as for normal NMR analysis.

Analysis:

$$\text{Hydroxyl content} = 45.25 \frac{A \cdot W_2}{B \cdot W_1} \text{ m equivs/g}$$

Where

- 45.25 = the milliequivs/g of polyethylene glycol 4000
- W₂ = the exact weight of polyethylene glycol (g)
- W₁ = the exact weight of polybutadiene (g)
- A = the integral of the carbons directly bonded to the oxygen in the polybutadiene (57.9, 63.1 and 64.6 ppm, due to cis-, trans- and vinyl units respectively)
- B = the integral of the carbons directly bonded to the oxygen in the polyethylene glycol (70.2 ppm).

B.3. Titrametric Method for the Determination of Isocyanate Equivalent Weight

This test method determines the isocyanate content of crude or modified isocyanates. Samples should be stored and handled under dry air or nitrogen to avoid moisture contamination.

The following solutions are required:

1. 2N dibutylamine in toluene (dry over sieves).
2. 1N hydrochloric acid in methanol (standardised).

Procedure:

1. Add 25 mL of dry 1,2,4-trichlorobenzene to a dry 250 mL wide-mouth conical flask.
2. Pipette 20 mL of the dibutylamine solution into the flask. Swirl to mix.

3. Add the required amount of isocyanate (calculated from the equation below).

$$\text{Weight of sample (g)} = \frac{84}{\text{expected \% NCO}}$$

4. Cover the flask and swirl the contents until the solution is homogeneous. The reaction mixture will warm up to approximately 40°C.
5. Let the mixture cool to room temperature (20-25 min), then add 100 mL of methanol.
6. Titrate with 1.0 N methanolic HCl:
- Potentiometrically, to the break that occurs at about pH 4.2 to 4.0. Titrate a blank (prepared exactly as above without adding the isocyanate).
 - Conventionally, using a bromophenol blue indicator (0.04% aqueous). Titrate until the first appearance of a stable yellow colour. Titrate a blank (prepared exactly as above without adding the isocyanate).

Calculations

$$\% \text{NCO} = \frac{4.202 (B-S)N}{W}$$

Where

- B = HCl required for titration of blank, mL
- S = HCl required for titration of sample, mL
- N = normality of HCl, meq/mL
- W = weight of sample, g
- 4.202 = constant combining the equivalent weight of NCO (42.02 mg/meq), conversion of g to mg (/1000) and conversion to % (x100).

Appendix C: Sample Calculations

Data: (typical values)

EW HTPB (R-45HT)	1101	EW IPDI	111
EW DHE	112	EW N-100	191
EW HTPE	1501		

Q1.

Calculate the percentage of HTPB and IPDI in an explosive formulation given:

DOA content	7.25%	Total binder content	16.00%
AO content	0.15%	NCO:OH	1.0/1

A.

$$\% \text{ Curatives (C)} = 16.00 - 0.15 - 7.25 = 8.60\%$$

Equivalents of HTPB = equivalents of IPDI

$$\% \text{ HTPB in formulation} = \frac{\text{EW (HTPB)}}{\text{EW(HTPB)} + \text{EW (IPDI)}} \times \% \text{C}$$

$$= 1101 / (1101 + 111) \times 8.60$$

$$= 1101 / 1212 \times 8.60 = 7.81\%$$

$$\% \text{ IPDI in formulation} = \frac{\text{EW (IPDI)}}{\text{EW(HTPB)} + \text{EW (IPDI)}} \times \% \text{C}$$

$$= 111 / (1101 + 111) \times 8.60$$

$$= 111 / 1212 \times 8.60 = 0.79\%$$

Q2.

Calculate the percentage of HTPB and IPDI in an explosive formulation given:

DOA content	7.25%	Total binder content	16.00%
AO content	0.15%	NCO:OH	1.2/1

A.

$$\% \text{ Curatives (C)} = 16.00 - 0.15 - 7.25 = 8.60\%$$

Equivalents of IPDI = 1.2 x equivalents of HTPB

$$1 \chi + 1.2 \chi = 8.60\%$$

$$\% \text{ HTPB in formulation} = \frac{1\text{EW (HTPB)}}{1\text{EW(HTPB)} + 1.2\text{EW (IPDI)}} \times \%C$$

$$= 1101 / (1101 + 1.2 \times 111) \times 8.60$$

$$= 1101 / 1234.2 \times 8.60 = 7.67\%$$

$$\% \text{ IPDI in formulation} = \frac{1.2\text{EW (IPDI)}}{1\text{EW(HTPB)} + 1.2\text{EW (IPDI)}} \times \%C$$

$$= 1.2 \times 111 / (1101 + 1.2 \times 111) \times 8.60$$

$$= 133.2 / 1234.2 \times 8.60 = 0.93\%$$

Q3.

Calculate the percentage of HTPB and IPDI in an explosive formulation given:

DOA content	7.45%	Total binder content	16.00%
AO content	0.10%	NCO:OH	1.0/1
Amount of DHE in formulation = 0.26%			

A.

$$\%C = 16.00\% - 0.10\% - 7.45\% = 8.45\%$$

IPDI = 1 equiv.

DHE + HTPB = 1 equiv.

Let DHE equiv. = χ , then HTPB equiv. = $1-\chi$

$$\% \text{ DHE in formulation} = \frac{\chi(\text{EW})}{\text{Total EW}} \times \%C = 0.26\% \text{ (given)}$$

$$\frac{\chi(112) \times 8.45\%}{1(111) + \chi(112) + (1-\chi)(1101)} = 0.26\%$$

$$\frac{946.4\chi}{1212-989\chi} = 0.26$$

$$946.4\chi = 315.12 - 257.14\chi$$

$$\chi = 0.262$$

$$\% \text{ HTPB} = \frac{(1-\chi)1101 \times 8.45\%}{1(111) + \chi(112) + (1-\chi)(1101)} = 7.21\%$$

$$\% \text{ IPDI} = \frac{1(111) \times 8.45\%}{1(111) + \chi(112) + (1-\chi)(1101)} = 0.98\%$$

Q4.

Calculate the percentage of HTPE and IPDI in an explosive formulation given:

DOA content	7.50%	Total binder content	17.00%
AO content	0.15%	NCO:OH	1.0/1
N-100 in formulation = 0.49%			

A.

$$\%C = 17.00\% - 0.15\% - 7.50\% = 9.35\%$$

HTPE = 1 equiv.

N-100 + IPDI = 1 equiv.

Let N-100 equiv. = χ , then IPDI equiv. = $1-\chi$

$$\% \text{ N-100 in formulation} = \frac{\chi(\text{EW})}{\text{Total EW}} \times \%C = 0.49\% \text{ (given)}$$

$$\frac{\chi(191) \times 9.35\%}{1(1501) + \chi(191) + (1-\chi)(111)} = 0.49\%$$

$$\frac{1785.85\chi}{1612 + 80\chi} = 0.49$$

$$1785.85\chi = 789.88 + 39.2\chi$$

$$\chi = 0.452$$

$$\% \text{ HTPB} = \frac{(1-\chi)1501 \times 9.35\%}{1(1501) + \chi(191) + (1-\chi)(111)} = 8.52\%$$

$$\% \text{ IPDI} = \frac{\chi(111) \times 9.35\%}{1(1501) + \chi(191) + (1-\chi)(111)} = 0.34\%$$

Note: The calculations are not always this straight forward, as the amount of plasticiser is often related to the amount of polymer and needs to be varied. In cases such as these it is a matter of trial and error - estimate the required amounts and put these numbers into the calculations, then adjust accordingly. The formulation will then have to be trialled and further adjusted to give the optimised product.

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19. ABSTRACT Polymer bonded explosives (PBXs) consist of explosive components bound together by a polymeric binder. The most common binder systems in current PBXs are polyurethane based and contain plasticisers and other chemicals that alter processability, mechanical properties and chemical stability. This report details the history of PBX binders, components of polyurethane binder systems, their properties and the procedures for obtaining the ingredients, as well as the basics of formulation, testing and quality control. Also included are details of PBX formulations on which research has been undertaken at DSTO.					